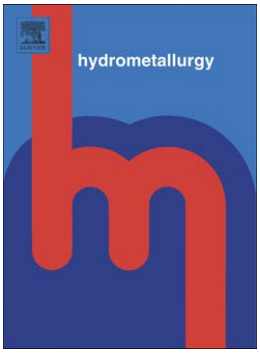

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The Anodic Behaviour of Chalcopyrite in Chloride Solutions: Potentiostatic Measurements

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Abstract

This paper summarizes the results of the first part of an electrochemical study of the anodic characteristics of chalcopyrite in the potential region relevant to ambient temperature heap leaching in chloride solutions during which both iron(II) and copper(II) act as oxidants for the mineral.

Mixed potential (E_m) measurements in concentrated chloride solutions in the presence of iron(II) or copper(II) have enabled the potential region of 0.65 V to 0.8 V to be defined as important in the leaching process. The systematic variations in E_m with pH and oxidant concentrations suggest that increases in both should result in increased rates of dissolution. This conclusion is also supported by simultaneous decreasing solution potentials due to reduction of the oxidants on the dissolving mineral surface. Slower rates of dissolution can be expected for iron(II) than copper(II) as the oxidant.

Potentiostatic measurements at various potentials in the above range at different pH values have confirmed that chalcopyrite undergoes a slow "passivation" that is not complete even after 24 hours. The current densities after prolonged oxidation vary exponentially with potential and increase with increasing pH but are not affected by the concentration of chloride in the range 1-5 M. Measurements with chalcopyrite samples from 3 different locations showed only minor variations in anodic reactivity.

Analysis of both the current-time transients and the re-activation of the mineral surface under zero current conditions after potentiostatic oxidation have been interpreted in terms of a growing copper-rich sulphide layer under anodic polarization. Solid-state diffusion through this layer is suggested as being responsible for the "passivation" process by analogy with the well known de-alloying and back-alloying processes in some binary alloys.

Keywords: chalcopyrite; electrochemistry; oxidation; passivation; mechanism

1. Introduction

As a result of the slow kinetics of leaching of chalcopyrite ($CuFeS_2$), a substantial amount of research work has been undertaken in order to understand the oxidative dissolution processes of this mineral. Most of this work has been aimed at increasing the oxidative dissolution kinetics in the presence of ferric ions as the oxidant in the sulfate system with the major overall reaction being

$$CuFeS_2 + 4Fe^{3+} = Cu^{2+} + 5Fe^{2+} + 2S^o \quad (1)$$

There are a large number of publications on this subject and reviews of these publications have been published (Burkin, 2001; Li et al., 2013).

It is now widely accepted that the slow rate of dissolution of chalcopyrite is not due to coating of the mineral surface with elemental sulphur or iron oxides. It has been proposed that the retardation in dissolution is the result of formation of a sulphide layer that is less reactive than chalcopyrite (Ammou-Chokroum et al, 1977; Parker et al., 1981; Warren et al., 1982; Barriga-Mateos et al., 1987; Hackl et al., 1995; Lundstrom et al, 2011). According to this theory (Burkin, 2001), this sulfide layer consists of ternary sulfides that are chemically and structurally different from the chalcopyrite from which they originated. These intermediate reaction products result from solid-state transformations which in turn are caused by the different dissolution rates of the cations leading to a change in the chemical composition of the residual sulfide phase.

The characteristic rapid decay in the anodic current for oxidation of chalcopyrite at potentials in the region of the mixed potential under typical leaching conditions i.e. below the so-called critical potential has been superficially investigated (Parker et al, 1981; Lu et al, 2000; Lazaro and Nicol, 2003) and interpreted by the last authors in terms of a model which is very similar to that found for the de-alloying process in many binary alloys. In terms of this mechanism, a relatively rapid initial but selective dissolution of the iron from chalcopyrite results in the formation of a less reactive copper-rich surface layer. Further dissolution is inhibited by relatively slow solid-state diffusion of copper and iron through this microscopically thin layer.

In recent studies (Velásquez et al., 2010ab) aimed at heap leaching of copper ores containing chalcopyrite under ambient conditions in chloride solutions of low (less than 1.5M) concentration, it was confirmed that the rate of chalcopyrite dissolution is enhanced in an optimum potential region similar to that initially observed by other authors in sulfate systems

(Kametani and Aoki, 1985; Hiroyoshi et al., 2000). A mechanism was proposed (Nicol et al., 2010) in which an intermediate covellite-like surface species is formed by non-oxidative dissolution of chalcopyrite by a reaction such as

$$CuFeS_2 + 2H^+ = CuS + Fe^{2+} + H_2S \quad (2)$$

and, in the presence of copper ions by a reaction such as

$$CuFeS_2 + Cu^{2+} = 2CuS + Fe^{2+} \quad (3)$$

Reaction (3) is similar to the well-known conversion of chalcopyrite that has been observed (Bartlett, 1992) at elevated temperatures and recently referred to as "covellinisation" (Muszer et al., 2013).

The reaction product layer formed in ferric and copper(II) chloride solutions of high concentration has generally been suggested to be a porous sulfur layer, which does not act as a diffusion barrier (Lundström et al., 2011). In ferric chloride media, iron precipitates as hematite at higher temperatures (> 100 °C) and as akaganeite (ß-FeOOH) at lower temperatures (Riveros and Dutrizac, 1997; Dutrizac and Riveros, 1999).

Recently, Lundström and coworkers (Lundström et al., 2008; 2009; 2011) have studied the dissolution behavior of chalcopyrite in concentrated (280 g/L NaCl) cupric chloride solutions at high temperatures (90^{o}C) and pH between 1.5 and 2.5 by means of electrochemical techniques, XRD analysis and microscopic methods. They observed that the pH value (from 1 to 3) of the concentrated cupric chloride solution significantly affected the dissolution rate of chalcopyrite, with the rate increasing with increasing pH. The results of their studies suggested that iron oxides, hydroxides and also elemental sulfur formed on the chalcopyrite surface at higher pH values while at lower pH values, chalcopyrite passivated and a sulfur-rich layer was detected on the surface.

As a result of the slow rates of dissolution, most leaching studies have been conducted at elevated temperatures and the results not directly applicable to heap leaching under ambient conditions (15-25^{o}C). More recent unpublished but patented research and development has demonstrated that direct oxidative dissolution of chalcopyrite can be successfully used in column and crib leaching of ores containing primarily chalcopyrite by increasing the chloride concentration in conjunction with other operating modifications. (Patino et al, 2014). This paper is part of a project aimed at a fundamental understanding of the kinetics of the leaching of chalcopyrite under such conditions. Although the focus is on concentrated chloride

solutions, it is likely that the conclusions would apply semi-quantitatively to other media such as sulfate.

2. Experimental

Several high purity chalcopyrite mineral samples have been used in this study, originating from Mt Isa Mines (Australia), Hezhang Guizhou (China), Ani Mine Akita (Japan) and Messina (South Africa). Unless stated otherwise, all experiments were conducted using the sample from China. All samples were identified as alpha chalcopyrite by using XRD analyses. Each sample was fabricated into a roughly cylindrical electrode using silver epoxy as the contact between the mineral and a stainless steel stud both of which were encased in epoxy resin. The platinum disk electrode was similarly fabricated from pure platinum rod with a diameter of 2 mm.

The base electrolyte was 5 M NaCl to which was added various amounts of 1 M HCl to adjust the pH to about 0, 1, 2, or 3. In some experiments cupric chloride or ferric chloride was added to the chloride solution. For the preparation of the electrolyte, analytical grade reagents HCl, $CuCl_2.2H_2O$, $FeCl_3.xH_2O$ and NaCl were used with de-ionized water.

Electrochemical measurements were performed using a standard three electrode system with a rotating electrode stand and a 100-mL double jacketed glass cell maintained at 25 °C by circulation of water from a thermostatted water bath. Unless stated otherwise, the electrode was rotated at 500 rpm. The chalcopyrite electrode was used as the working electrode and a silver/silver chloride electrode (3MKCl) as the reference. A coiled platinum wire, used as the counter electrode, was housed in a glass tube with a glass frit at the bottom to separate the electrode from the bulk solution in cell. A combined Pt/calomel electrode (saturated KCl) was used for measuring the solution potential of the electrolyte.

Electrochemical experiments were carried out using either an EG&G Princeton Applied Research (PAR) Model 173 potentiostat or a BAS model CV-27 potentiostat. Analogue data from the potentiostats were collected using a National Instrument data acquisition board controlled by LabView^{TM} software.

Before all experiments, the electrolyte (about 30 - 40 ml) was maintained at 25 °C with a water bath for at least 20 minutes. When de-aeration was required, high purity nitrogen gas was bubbled through the solution. A fresh chalcopyrite electrode surface was prepared by wet-grinding using #1200 emery paper followed by ultrasonically cleaning in water, rinsing

with de-ionized water and drying in air before placing in the cell. The electrode was maintained at the open circuit potential before the potential was set to a predetermined value for the desired time. No corrections for uncompensated ohmic drops were made due to the low currents involved. All potentials reported are quoted with respect to the standard hydrogen electrode (SHE). After the potentiostatic experiments, selected solutions were analysed after dilution for dissolved copper and iron ions by ICP-MS.

3. Results and Discussion

3.1 Mixed Potential Measurements

In order to establish the potential range of importance during oxidative leaching of chalcopyrite in chloride solutions, measurements were made of the potentials of both chalcopyrite and platinum electrodes at various pH values in aerated 5 M NaCl solutions containing various concentrations of copper(II) or iron(III) at 25 ^{o}C.

The results are shown in Figures 1 to 3 for solutions containing copper(II) ions which show that the mixed potentials increase with time with a reasonably steady value achieved more rapidly at the higher pH values. The increase is due to decreasing (with time) anodic currents that, according to the mixed potential model, will result in increasing potentials with time of oxidation. On the other hand, the solution potentials decrease with time due to reduction of copper(II) ions by the mineral and production of copper(I) ions from the dissolution of the mineral by reactions such as

$$CuFeS_2 + 3Cu(II) = 4Cu(I) + Fe(II) + 2S \qquad (4)$$

The greater decrease in the solution potential at higher pH values indicates that the rate of dissolution with copper(II) as an oxidant should increase with increasing pH. The difference between the mixed and solution potentials decreases with time and is between 40mV and 65mV after 1 hour depending on the pH. The higher mixed potentials at higher copper(II) concentrations suggest that the rate of dissolution by reaction (4) should increase with increasing copper(II) concentration.

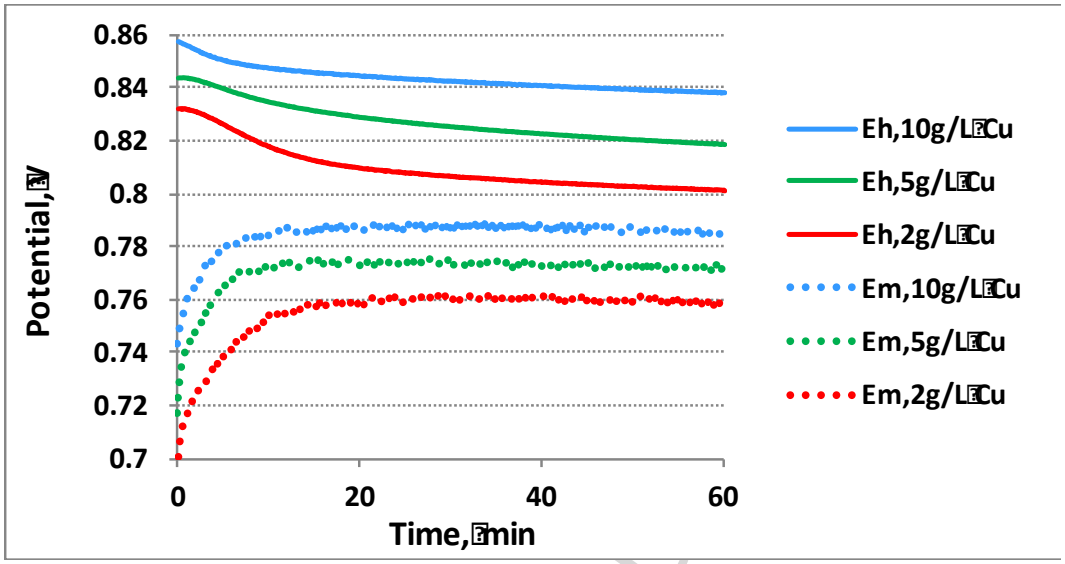

Figure 1. Chalcopyrite mixed (Em) and solution (Eh) potentials at pH 1 in aerated solutions of 5 M NaCl containing various concentrations of copper(II).

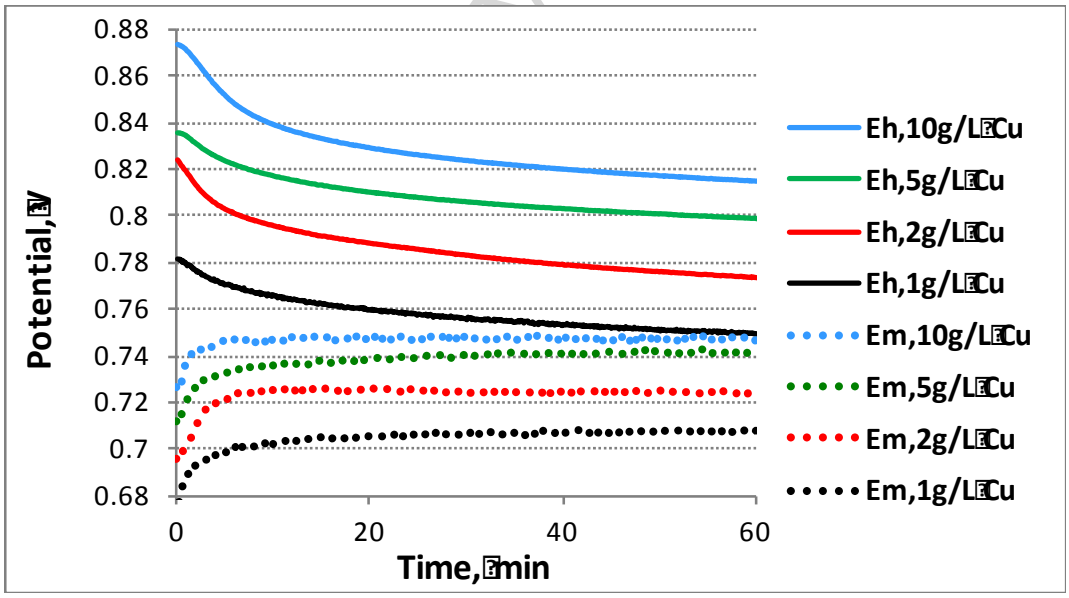

Figure 2. Chalcopyrite mixed (Em) and solution (Eh) potentials at pH 2 in aerated solutions of 5 M NaCl containing various concentrations of copper(II).

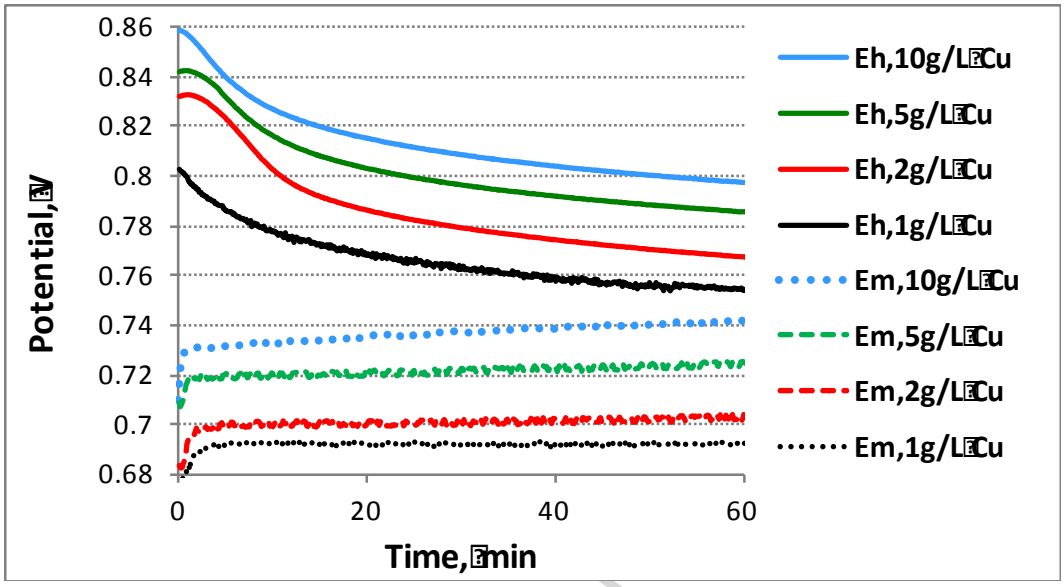

Figure 3. Chalcopyrite mixed (Em) and solution (Eh) potentials at pH 3 in aerated solutions of 5 M NaCl containing various concentrations of copper(II).

The corresponding data obtained in the presence of iron(III) at pH 1 is shown in Figure 4. It is not possible to prepare solutions of iron(III) at concentrations greater than about 1 g/L at higher pH values due to precipitation of iron. The data in Figure 5 summarizes the results obtained at higher pH values with 1 g/L iron(III)

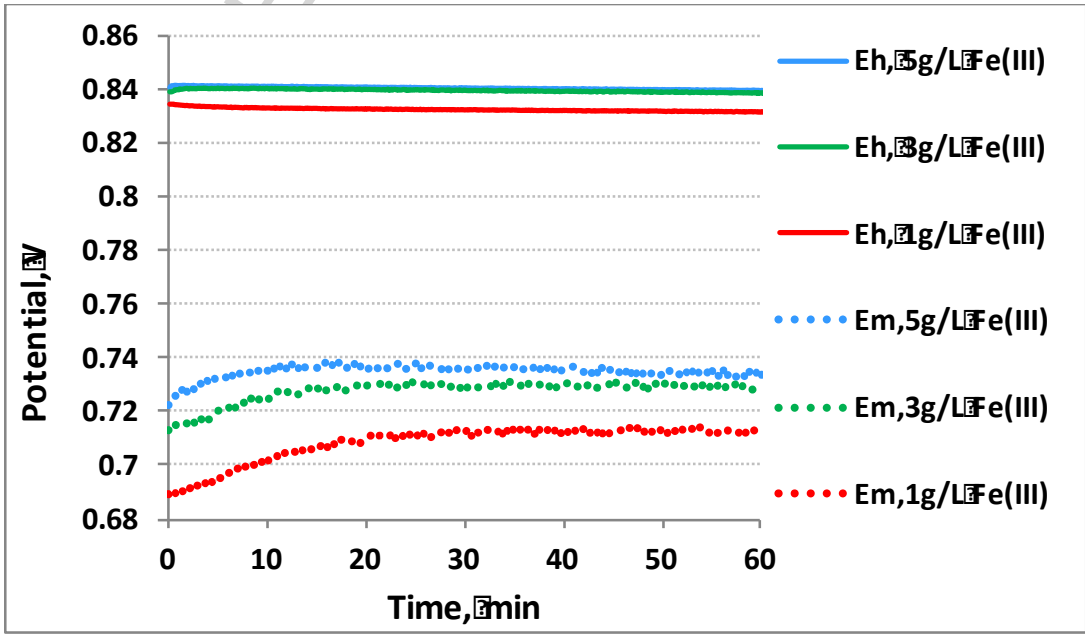

Figure 4. Chalcopyrite mixed (Em) and solution (Eh) potentials at pH 1 in aerated solutions of 5 M NaCl containing various concentrations of iron(III).

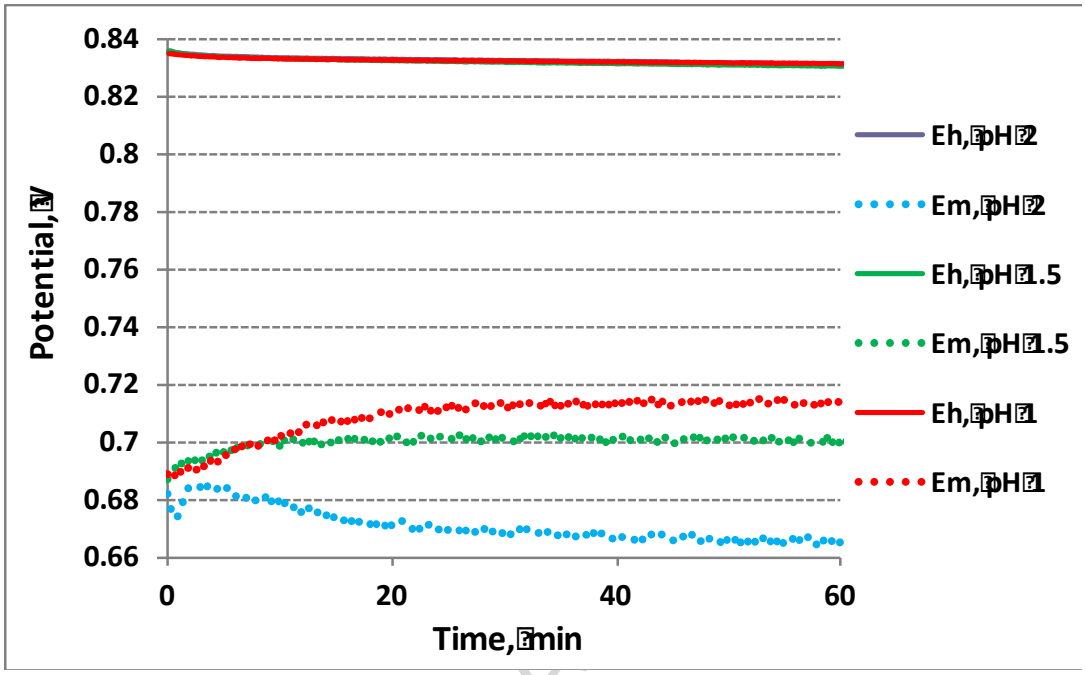

Figure 5. Chalcopyrite mixed (Em) and solution (Eh) potentials at various pH values in aerated solutions of 5 M NaCl containing 1 g/L iron(III).

The almost constant (with time) solution potentials are indicative of the slower rate of oxidation of chalcopyrite by iron(III) than copper(II) under these conditions and also due to the lower sensitivity of the potential to the production of small amounts of iron(II) than copper(I) as a result of the greater formal potential of the iron(III)/iron(II) couple (0.595 V) than the copper(II)/copper(I) couple (0.565 V) under these conditions. As in the case of copper(II), the increasing mixed potentials are indicative of slow "passivation" of the anodic reaction. The decreasing mixed potential at pH 2 is due to slow precipitation of some iron(III).

These results serve to identify the potential region of about 0.65 V to 0.80 V as important in the dissolution of chalcopyrite under these conditions and indicative for further study of the electrochemistry. These results also highlight the differences to be expected in practice between the solution potential (measured) and the actual potential on the mineral surface that is not measured during practical leaching of the mineral.

3.2 Potentiostatic Experiments in 5 M NaCl solutions

In order to investigate the steady-state anodic characteristics of chalcopyrite, potentiostatic experiments were conducted in which the potential of the mineral was fixed at values selected

on the basis of the mixed potential measurements and the current followed as a function of time. Initial experiments were conducted over 4 hours and a limited set then carried out over 24 hours.

3.2.1 Current-time transients over 4 hours

Potentiostatic experiments were carried out in de-aerated 5 M NaCl solutions at 25 ^{o}C at pH values of 1, 2 and 3 by applying constant potentials in the range of 0.65 to 0.85 V to a stationary China chalcopyrite electrode for a period of four hours. The anodic currents were recorded and the solutions analysed after four hours for dissolved copper and iron by ICP-MS. Figures 6 to 8 show the resulting current/time transients at various potentials and pH values.

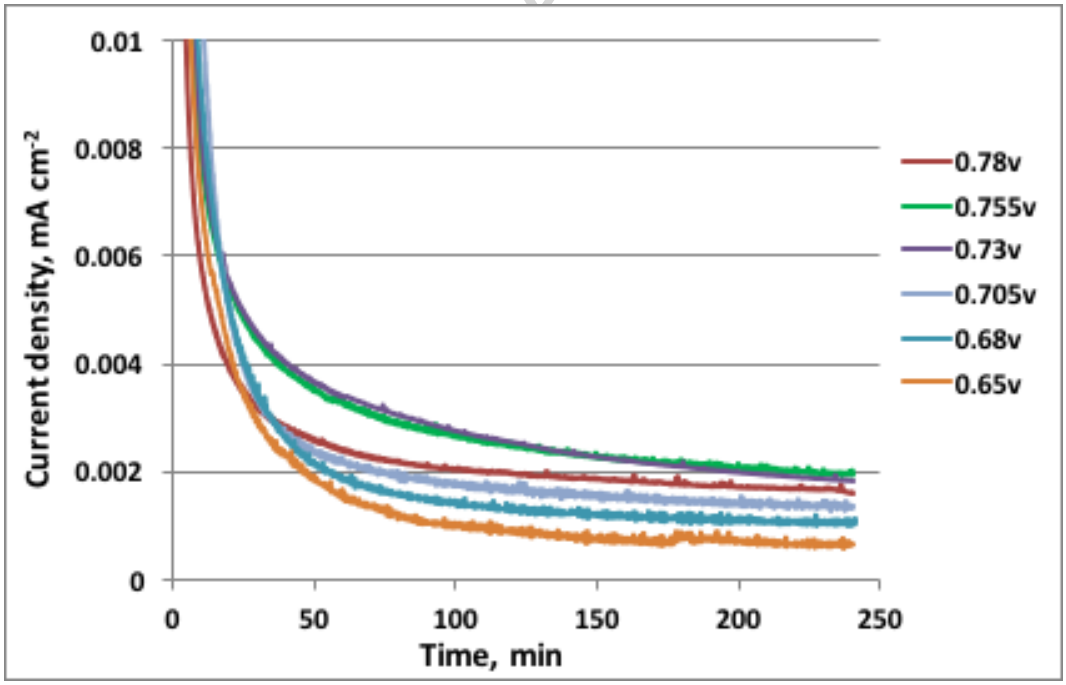

Figure 6. Current-time transients for a China chalcopyrite electrode at various potentials in deaerated 5 M NaCl solutions at pH 1.

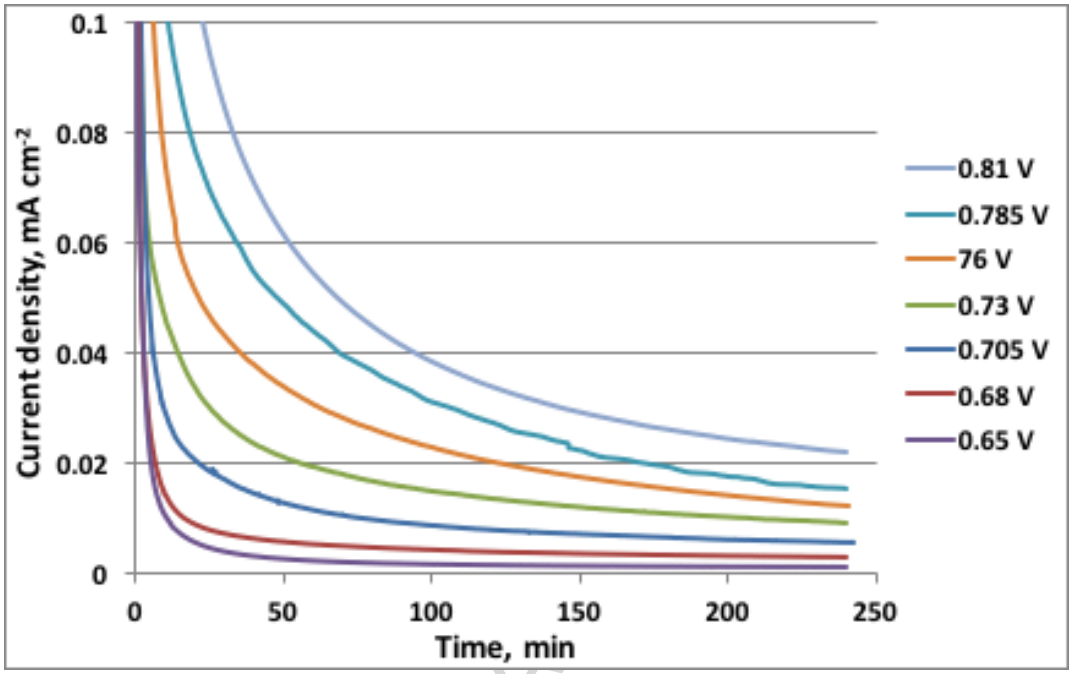

Figure 7. Current-time transients for a China chalcopyrite electrode at various potentials in de-aerated 5 M NaCl solutions at pH 2.

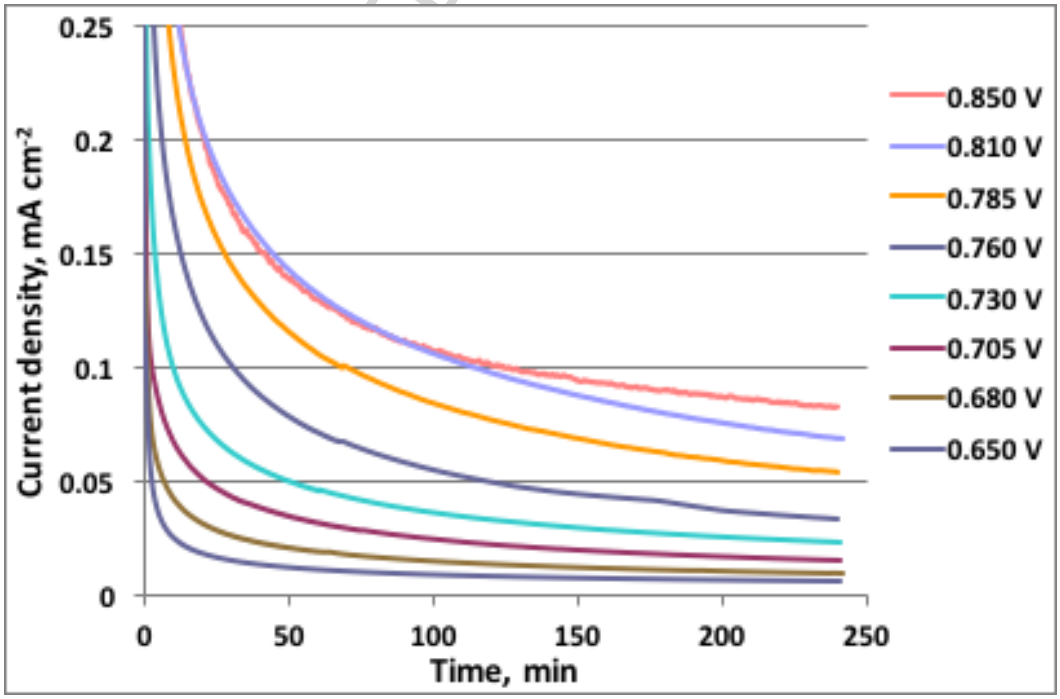

Figure 8. Current-time transients for a China chalcopyrite electrode at various potentials in de-aerated 5 M NaCl solution at pH 3.

It is apparent that at all potentials and pH values the currents decrease gradually with time and do not achieve steady-state values even after 4 hours. The pH significantly affects the

current after 4 hours (compare ordinate scales) with the current being higher at higher pH values within the range studied. Except at potentials above about 0.75V at pH 1 in 5M NaCl solution where the current after four hours is lower than at the lower potentials, there is no evidence of typical passivation behaviour. The effect of potential on the anodic current depends on the solution pH and the effects of pH and applied potential will be analysed in a subsequent section as will the shapes of the transients.

The results of similar experiments (results not shown here) conducted in 3M NaCl solutions at different pH values showed very little difference in the currents at the same potentials used for the experiments with 5M NaCl solutions. In agreement with this, the data shown in Figure 9 for a Mt Isa electrode shows that the concentration of NaCl has no observable effect on the potentiostatic response at 0.705V in solutions of pH 1.

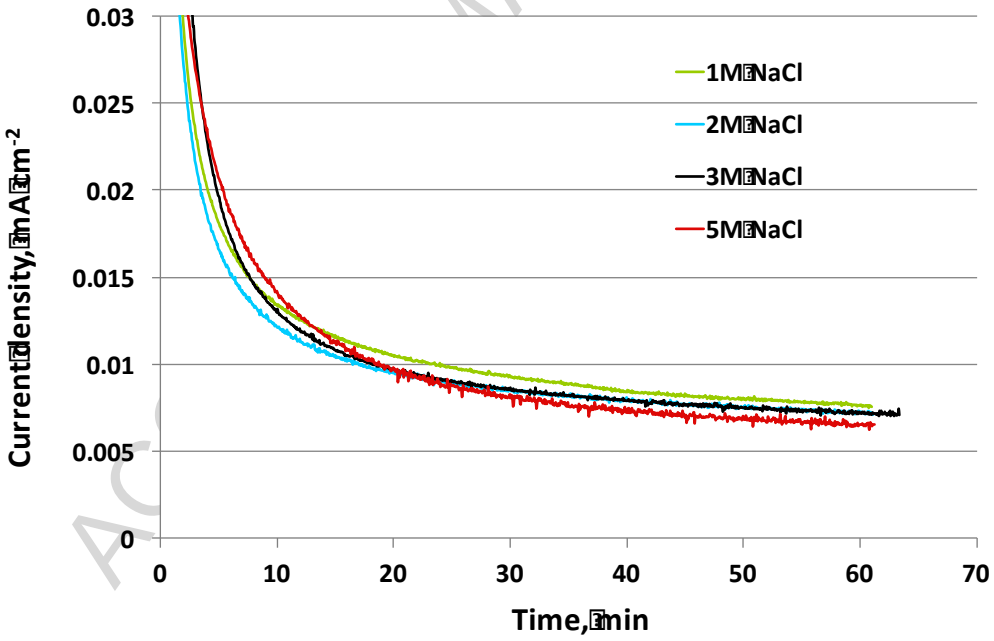

Figure 9. Current-time transients for a Mt Isa chalcopyrite electrode at 0.705 V in solutions of various concentrations of NaCl at pH 1.

The surface of the chalcopyrite electrode after 4 hours potentiostatic oxidation was viewed using optical microscopy. The electrode surface appeared largely unchanged after oxidation in solutions of pH 1 at all potentials. At pH 2 and 3, the chalcopyrite surface was covered by brown, blue and/or grey areas depending on the potential. With increasing potential the surface changed from brown to blue/grey. The amount of visible surface coverage appeared to be greater at pH 3 than at pH 2. It was also found that the grey material can be dissolved by

a drop of carbon disulphide suggesting the presence of elemental sulphur as expected on the surface. The brown material indicates the presence of iron hydroxides particularly at the higher pH while the blue areas may suggest the presence of "covellite-like" phases.

3.2.2 Current-time transients over 24 hours

Similar potentiostatic experiments were carried out in aerated 5 M NaCl solutions at 25 ^{o}C at pH values of 1, 2 and 3 by applying constant potentials of 0.65, 0.75 and 0.85 V to a stationary China chalcopyrite electrode for 24 hours. The current was recorded and solutions analysed for dissolved copper and iron by ICP-MS. In these experiments 5 mL of the solution was withdrawn after 8 hours and the dissolution rates of copper and iron were based on the analyses of samples after 8 hours and 24 hours. Figures 10 to 12 show the resulting current-time transients at various potentials and pH values. The dotted lines are calculated curves based on the analysis described below.

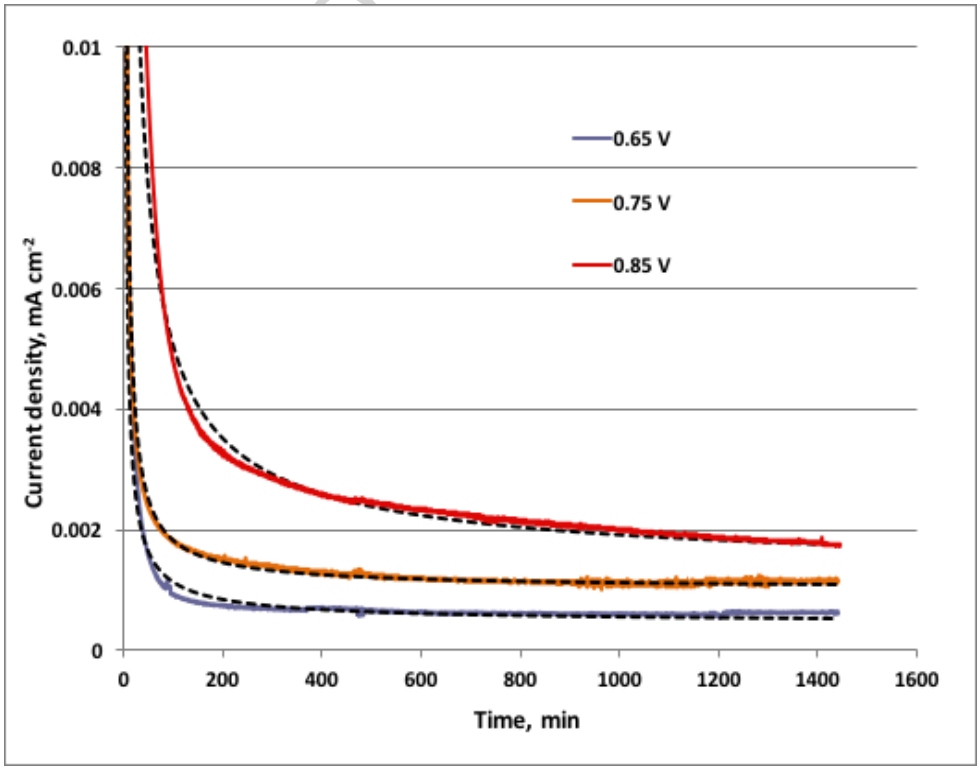

Figure 10. Current-time transients over 24 hours for a China chalcopyrite electrode at various potentials in aerated 5 M NaCl solutions at pH 1.

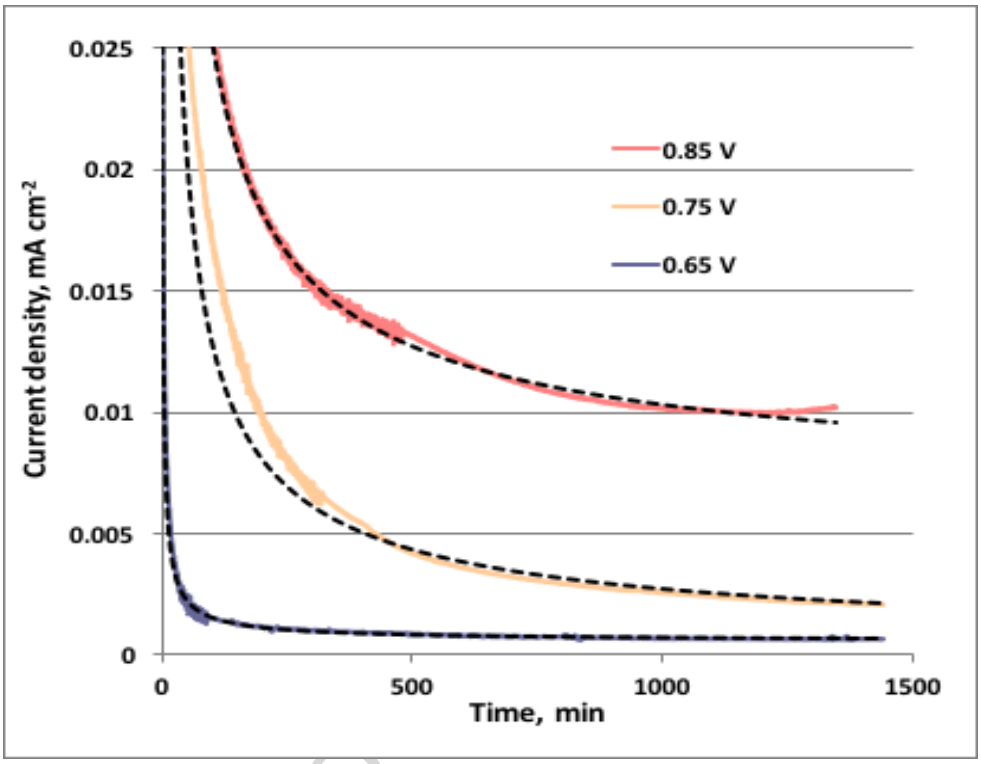

Figure 11. Current-time transients over 24 hours for a China chalcopyrite electrode at various potentials in aerated 5 M NaCl solutions at pH 2

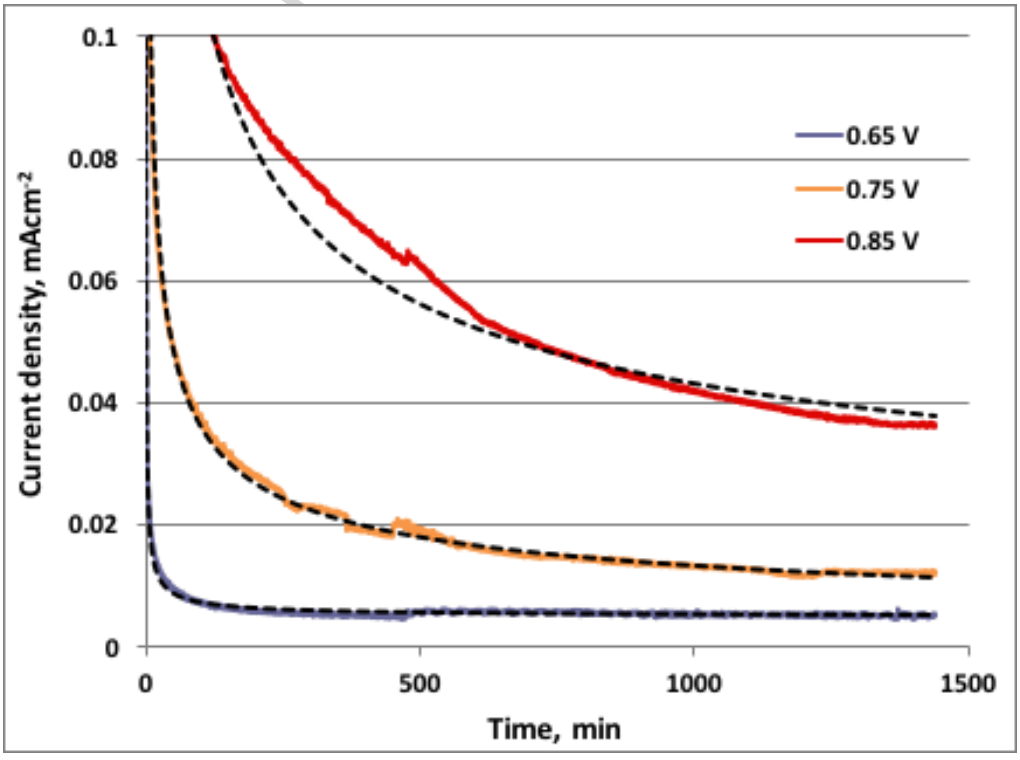

Figure 12. Current-time transients over 24 hours for a China chalcopyrite electrode at various potentials in aerated 5 M NaCl solutions at pH 3.

It can be seen that even after 24 hours the anodic currents are still decreasing gradually with time particularly at the higher pH values Thus, any analysis of the anodic reactivity of chalcopyrite must take into account that "passivation" is an extremely slow process that does not have the characteristics of classic passivation reactions. The currents after 24 hours increase with increasing potential at all pH values and with increasing pH at a fixed potential.

The currents at 4, 8 and 24 hours are plotted in Figures 13 to 15. In all cases, the lines drawn are exponential fits of current density as a function of potential. The pseudo-steady-state Tafel slopes obtained from the exponential fits vary from a low of 169 mV/decade at pH 2 after 24h to a high of 440 mV/decade after 4h at pH 1 with no discernible trends with pH or time. Thus, little mechanistic information can be obtained from the values of these slopes which are, in any event, calculated from only 3 points.

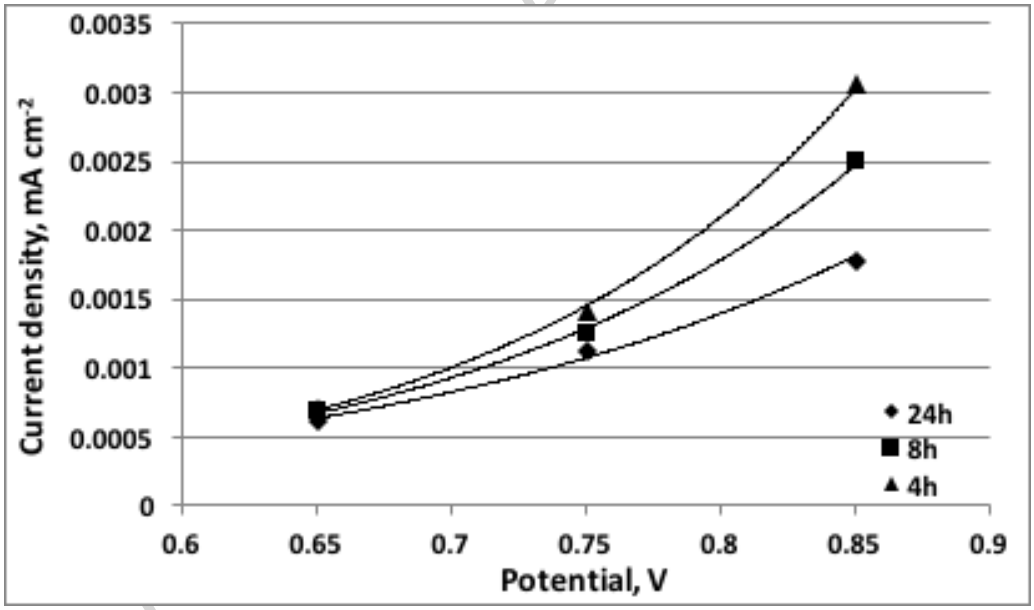

Figure 13. Anodic current-potential curves at various times on a stationary China chalcopyrite electrode in aerated 5 M NaCl solution at pH 1.

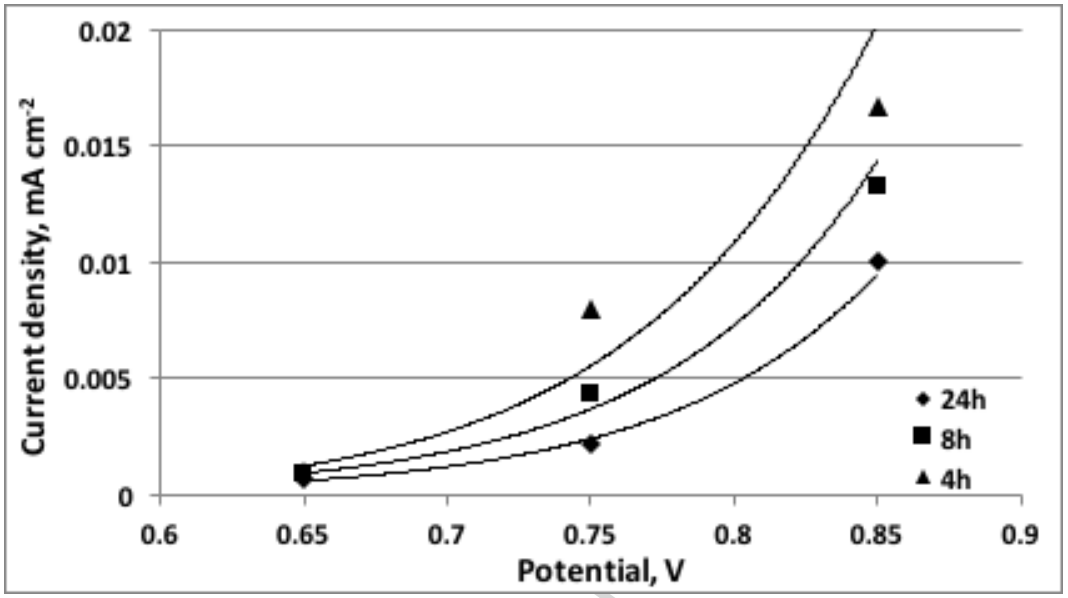

Figure 14. Anodic current-potential curves at various times on a stationary China chalcopyrite electrode in aerated 5 M NaCl solution at pH 2.

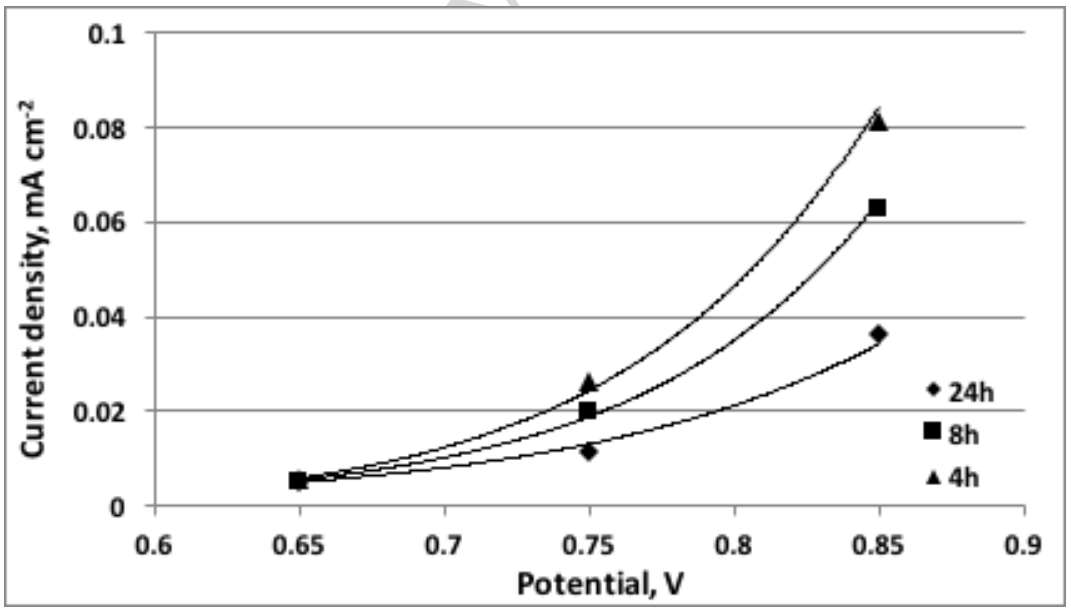

Figure 15. Anodic current-potential curves at various times on a stationary China chalcopyrite electrode in aerated 5 M NaCl solution at pH 3.

3.2.3 Coulometric measurements

Additional information on the nature of the dissolution and "passivation" processes can be obtained from measurements of the average stoichiometry of the anodic reactions. Thus, the total charge passed over periods of 4, 8 and 24 hours can be compared with the amounts of copper and iron dissolved as measured by analysis of the solutions.

The data obtained at various potentials and pH values in 5M NaCl solutions after 4 hours is shown in Figure 16 as the ratio of the stoichiometric number of electrons (expressed as the charge in Faradays) to the number of moles of copper dissolved. It should be pointed out that these data are subject to some uncertainty given the difficulty of accurate chemical analysis of trace amounts of copper and iron in solutions of high ionic strength.

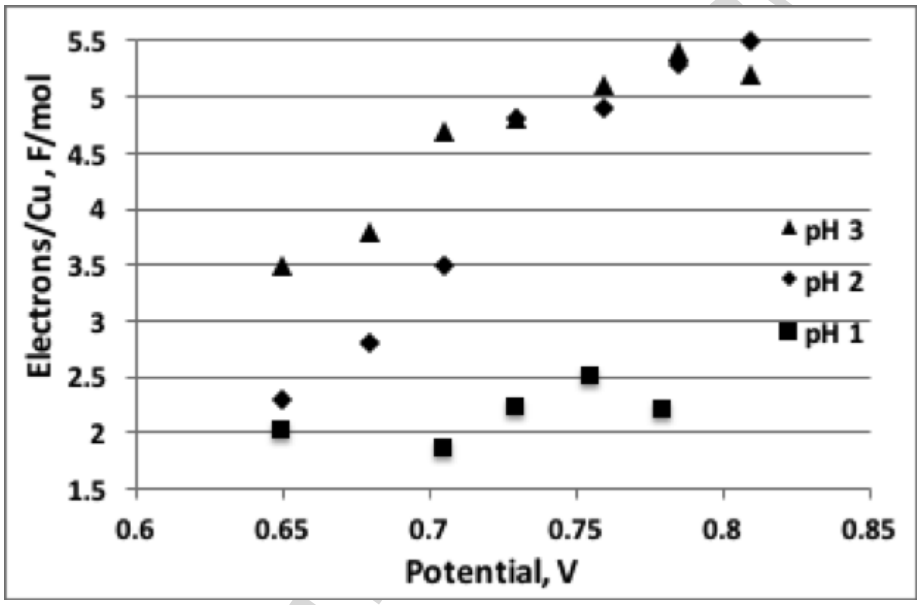

Figure 16. Average stoichiometry of anodic dissolution of copper over 4 hours in 5M NaCl solutions at various pH values

Similar data for experiments after 8h and 24h are shown in Figures 17 and 18. These data are probably more reliable than the above given the higher concentrations of copper and iron in solution after longer periods of oxidation. It appears that the average ratio over 4 hours is about 2 in solutions of pH 1. At the higher pH values, the ratio increases with increasing potential from about 2 to 5.5 at pH 2 and 3.5 to 5.4 at pH 3. After longer periods, the ratio increases with potential from 2.5 to 3.5 at pH 1, 3 to 5 at pH 2 and 4 to 5.5 at pH 3.

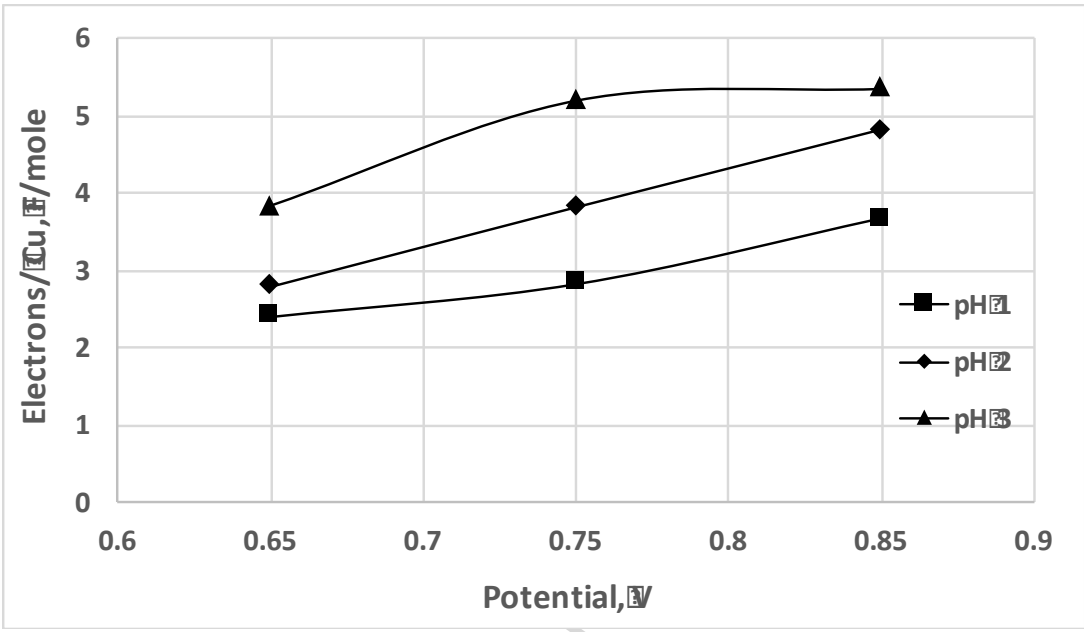

Figure 17. Average stoichiometry of anodic dissolution of copper over 8 hours in 5M NaCl solutions at various pH values.

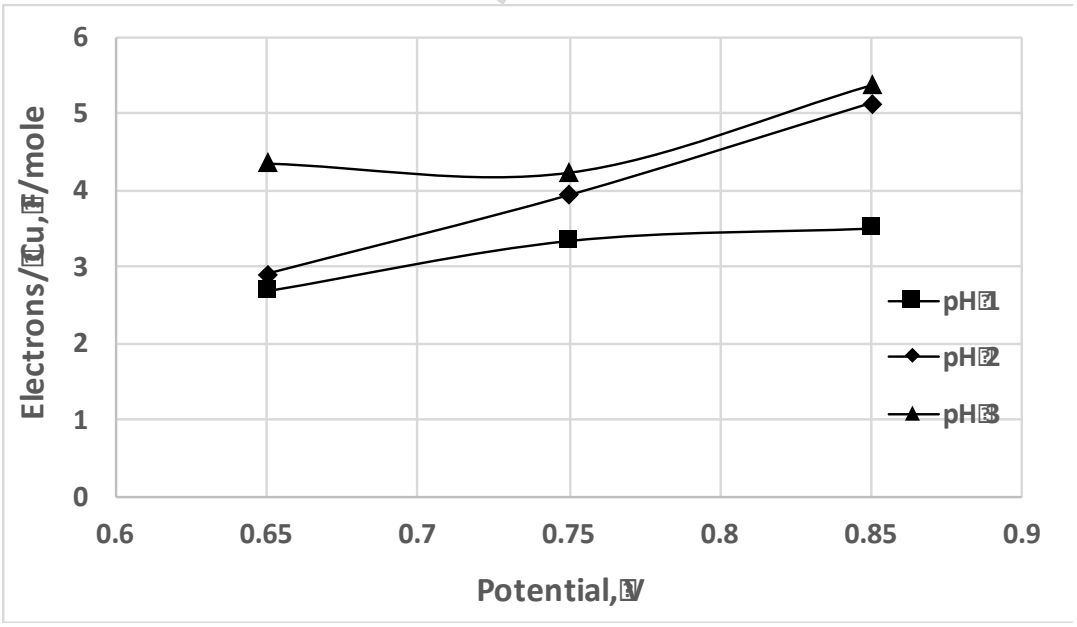

Figure 18. Average stoichiometry of anodic dissolution of copper over 24 hours in 5M NaCl solutions at various pH values

The generally accepted stoichiometric equations for the anodic dissolution of chalcopyrite in acidic solutions can be written in several forms depending on the oxidations states of the products. Thus, for elemental sulphur as the product of oxidation, the following can be written for chloride solutions

$$CuFeS_2 = Cu(I) + Fe(II) + 2S + 3e^- \qquad E_f = 0.295V \qquad (5)$$

$$CuFeS_2 = Cu(II) + Fe(II) + 2S + 4e^- \qquad E_f = 0.395V \qquad (6)$$

$$CuFeS_2 = Cu(II) + Fe(III) + 2S + 5e^- \qquad E_f = 0.450V \qquad (7)$$

The potentials shown are the formal potentials calculated for 5M NaCl solutions. In terms of these reactions, values of the e/Cu ratio cannot be lower than 3 or greater than 5. The ratio could be expected to increase with increasing potential given the increasing stability of the higher oxidation states of copper and iron at the higher potentials. This is generally observed in the above Figures. However, at pH 1 and pH 2 at low potentials, the amount of copper dissolved is in excess of that which can be accounted for by these reactions. This suggests that parallel reactions involving non-oxidative reactions such as reactions (8) or (9) could be involved at low pH values.

$$CuFeS_2 + 4H^+ = Cu(II) + Fe(II) + 2H_2S \qquad (8)$$

$$CuFeS_2 + 2H^+ = CuS + Fe(II) + H_2S \qquad (9)$$

These reactions have previously been suggested as relevant in the low potential leaching of chalcopyrite in dilute chloride solutions (Nicol et al, 2010). The more favourable equilibrium for reaction (9) suggests that this reaction is more likely than (8). Alternative reactions involving the formation of copper polysulfide species designated for simplicity as "CuS_2" in reaction (10) could also account for low Cu/e ratios.

$$CuFeS_2 = \text{“}CuS_2\text{”} + Fe(II) + 2e^- \qquad (10)$$

Biegler and Horne (1985) proposed (without direct stoichiometric experimental evidence) that at potentials below the critical potential the following reaction occurs in sulfate solutions

$$CuFeS_2 = 0.75CuS + 0.25Cu^{2+} + Fe^{2+} + 1.25S + 2.5e \qquad (11)$$

Reactions (9), (10) and (11) would result in dissolved iron/copper molar ratios greater than one. This additional information is available by comparing the molar ratios of dissolved iron to copper after dissolution and the results shown in Figures 19 to 21.

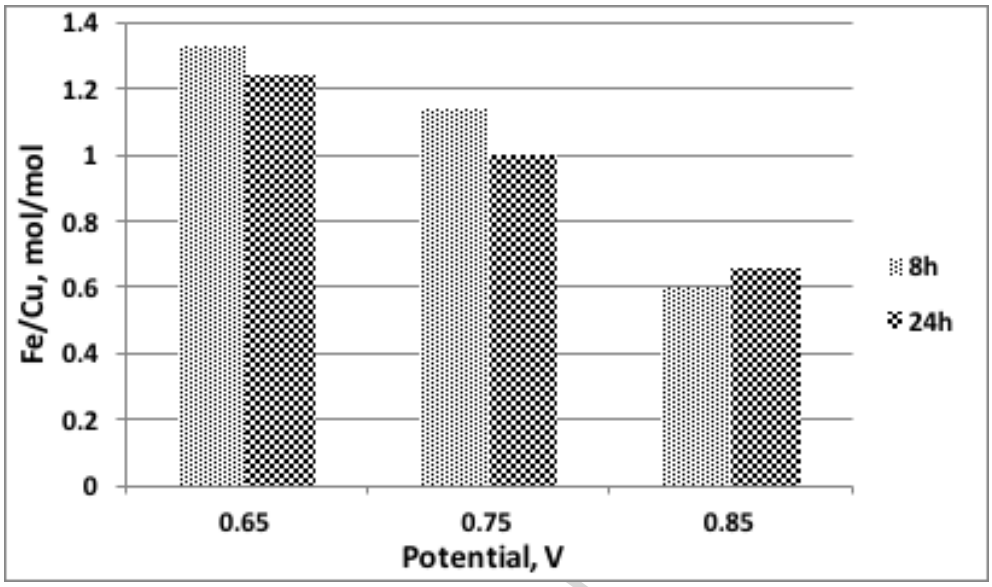

Figure 19. Molar ratios of dissolved iron to copper over 8 and 24 hours at various potentials in de-aerated 5 M NaCl solutions at pH 1.

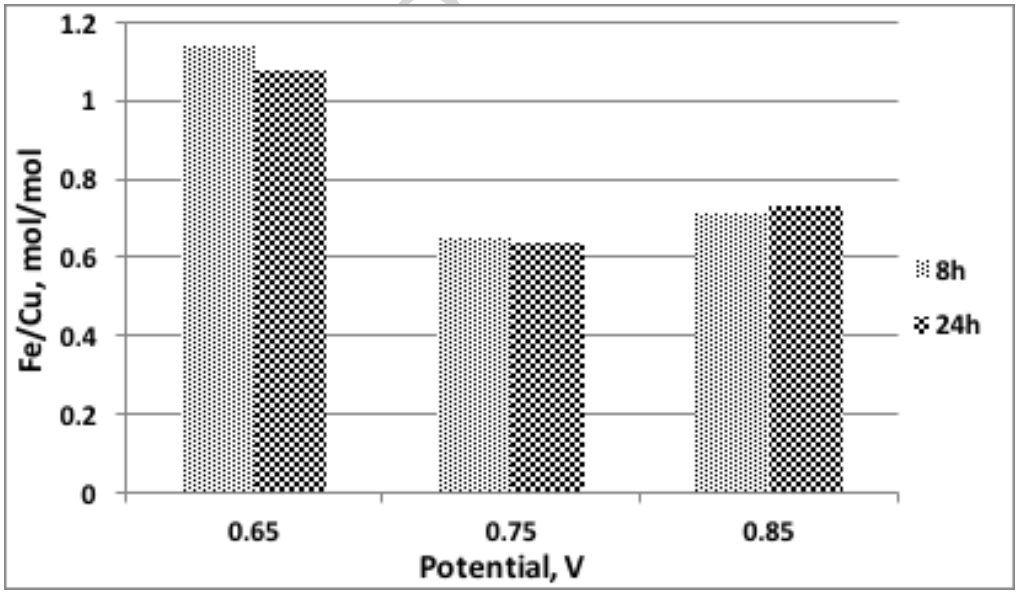

Figure 20. Molar ratios of dissolved iron to copper over 8 and 24 hours at various potentials in de-aerated 5 M NaCl solutions at pH 2.

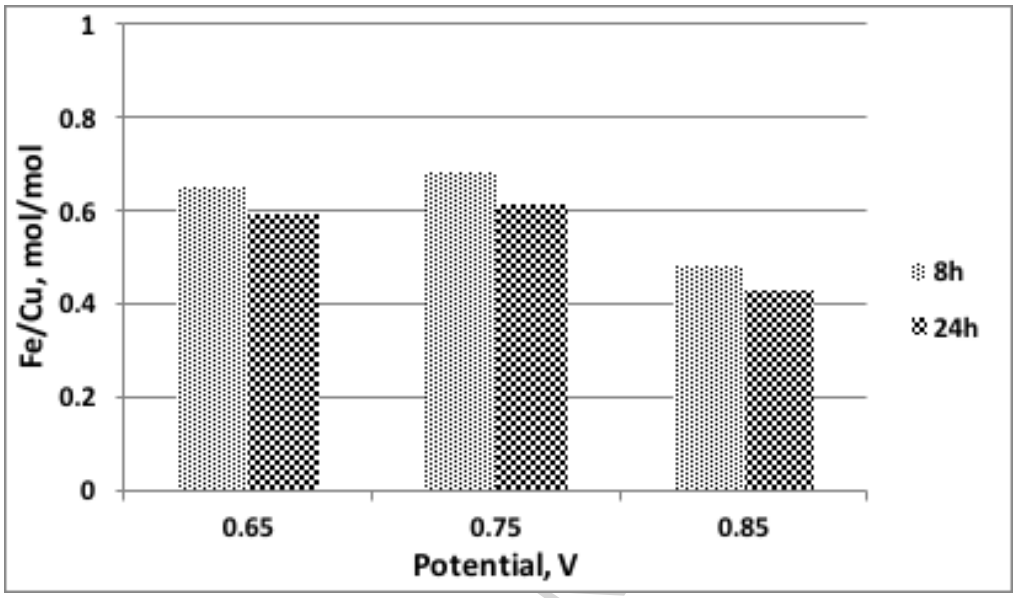

Figure 21. Molar ratios of dissolved iron to copper over 8 and 24 hours at various potentials in de-aerated 5 M NaCl solutions at pH 3.

Values of the ratio greater than 1 are consistent with the above suggestion that reactions such as shown in (9) or (10) are involved at low pH values and potentials. Thus, as has been previously suggested in the case of dissolution in sulphate solutions, partially selective dissolution of iron occurs that is more obvious during the early stages of dissolution. The decrease in the ratio of dissolved iron to copper with increasing pH suggests the formation of insoluble compounds such as iron hydroxides and/or basic iron(III) chlorides such as akaganite on the surface of chalcopyrite as observed visually after oxidation at high pH values. Given the greater reactivity at the higher pH values, it appears that the precipitated iron hydroxide is porous and therefore does not significantly inhibit the dissolution of chalcopyrite as suggested by Lunström et al. (2008).

4 Effect of the source of chalcopyrite

The anodic response of electrodes made from chalcopyrite samples from different sources were compared in potentiostatic experiments at the same potential and solution conditions. The results are shown in Figure 22. Given the uncertainties of the active surface areas of each electrode, the results indicate that the differences in behaviour are relatively small. This confirms previously published data obtained in sulphate solutions that suggests that chalcopyrite samples from different sources behave similarly in terms of leaching kinetics (Dutrizac, 1982).

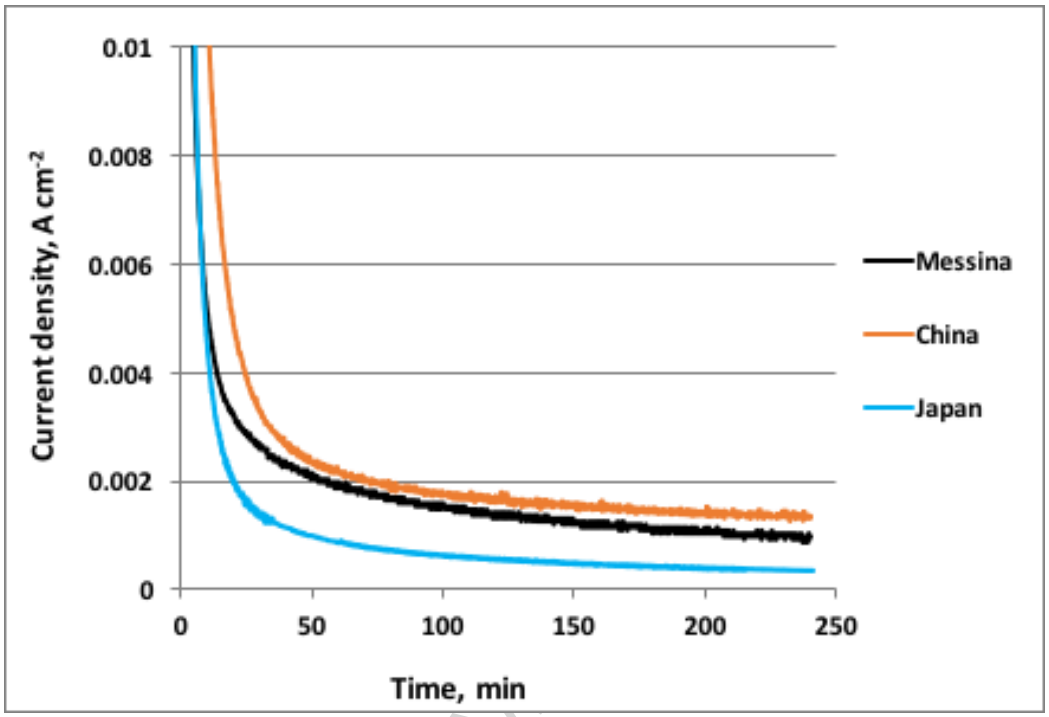

Figure 22. Current-time transients over 4 hours for different chalcopyrite electrodes in aerated 5 M NaCl solutions at pH 1 and a potential of 0.705V.

5 Mechanism of "passivation"

As summarized in the introduction, much has been published on the nature of the so-called passivation of chalcopyrite during dissolution in acidic solutions. It is important to emphasize that although the process has been termed passivation, under the conditions of the experiments conducted in this study, it is not a classical passivation process whereby the current decreases with increasing potential but involves a very slow decrease in anodic current with time at all potentials in the range 0.65 to 0.85V. Similar results have been obtained in sulphate solutions (Lazaro and Nicol, 2003; Pugaev et al, 2011). As will be demonstrated in a second paper based on voltametric studies, the commonly assumed association of a peak or shoulder on the anodic voltammogram with passivation is not true.

As noted in a previous publication (Lazaro and Nicol, 2003) the anodic characteristics of chalcopyrite are remarkably similar to those commonly observed for the anodic dissolution of some alloys such as those of copper-zinc and copper-gold. The reader is referred to a publication (Ateya et al, 2002) on the dissolution of copper-gold alloys for details and references to other published work in this area. In the case of these alloys, the polarization behaviour reveals low anodic current densities below a critical potential E_c, at which the

current rapidly increases with increasing potential. Selective dissolution of the less noble component occurs at potentials below E_c with enrichment of the surface with the more noble component. At potentials above E_c, non-selective dissolution occurs at rapid rates with noticeable pitting of the alloy surface. Chalcopyrite exhibits similar characteristics. In the subcritical potential region, the dissolution current density is found to be proportional to t^{-m} with $0.5<m<1.0$ for all alloys, electrolytes and potentials studied. A value of m of 0.5 indicates linear solid-state diffusion into the surface layer (similar to semi-infinite linear diffusion in solution as in the Cottrell equation) while, for surface diffusion, m = 1. The dotted lines in Figures 10 to 12 are fits of the function $i = i_{inf} + at^{-m}$ to the data. i_{inf} is the current density at infinite time while "a" is a constant. The fitted currents generally approximate the observed data and the calculated values of m vary between 0.49 and 0.87 depending on the conditions that suggests a combination of linear and surface diffusion is involved.

The mass of copper dissolved in the experiments summarized in Figures 10 to 12 varies from 0.5 to 10 μmol/cm^2 in 24 hours. Using the molar volume of chalcopyrite (43.9 cm^3 mol^{-1}) and assuming one mol of chalcopyrite dissolved per mol copper released, one can calculate that the extent of dissolution after 24 hours is equivalent to between 0.25 μm and 6 μm of the mineral. Given that the P1200 paper used for polishing the electrodes has a grit size of 15.3 μm, it is not surprising that both linear (normal to the surface) and surface (from the ridges in the scratch marks) diffusion processes are involved in the potentiostatic experiments with a value of the exponent m that depends on the density and height of the surface polishing marks.

As pointed out (Ateya et al, 2002) in a TEM study, the surface of a Cu-Au alloy became depleted in Cu during the (current on) selective dissolution process and then underwent a recovery (back alloying or homogenization) which started immediately upon cessation of current flow and continued for long periods during the open-circuit period. Typically hours or days passed before TEM examination and it is therefore not surprising that the TEM results showed a nearly homogeneous composition through the product layer.

This process of "back-alloying" occurs also in the case of chalcopyrite. Thus, by a process involving solid-state diffusion and re-arrangement, the surface of chalcopyrite recovers after anodic oxidation and the original reactivity is almost completely restored. This phenomenon has been previously noted qualitatively at higher temperatures (Parker et al, 1981; Lu et al, 2000) and quantitatively confirmed under the present conditions. Thus, a chalcopyrite

electrode was anodically oxidized for 1 hour at a potential of 0.65 V in 5M NaCl solution and the current transient is shown as the black curve in Figure 23.

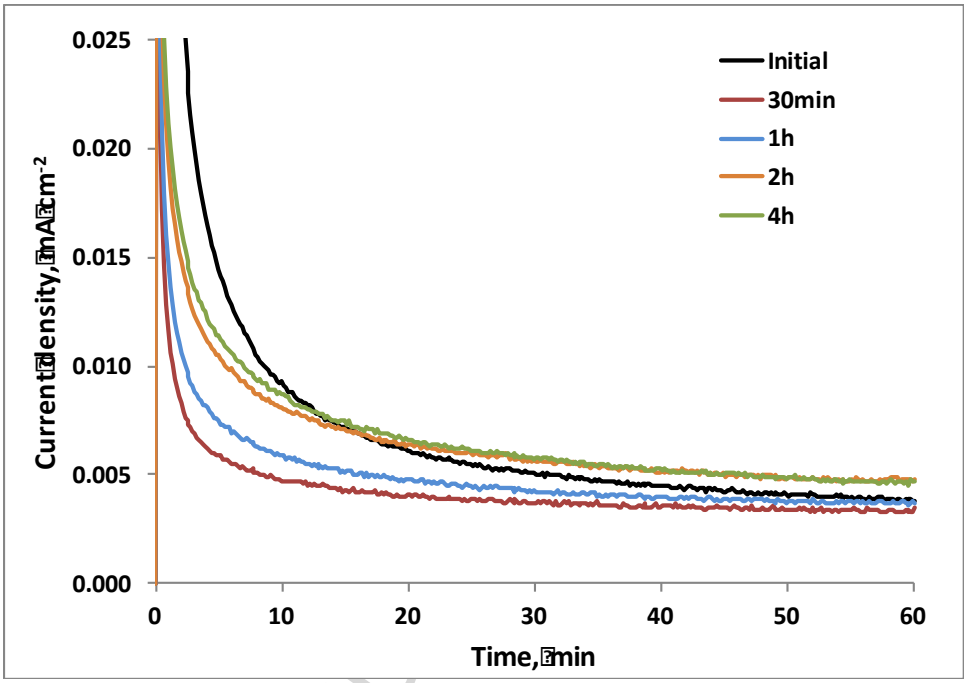

Figure 23. Effect of open-circuit period on current transients at 0.65V obtained after 1 hour at 0.65V in 5MNaCl at pH 3.

After oxidation, the electrode was placed under open-circuit in the solution for 30 minutes after which it was then oxidized again at 0.65 V. The resulting transient in also shown in Figure 23. The sequence was repeated with increasing periods of open-circuit between the potentiostatic periods and it is apparent that the anodic reactivity is slowly restored as the open-circuit period increases.

The charge (Q) under the transients shown in Figure 23 were obtained and a linear relation between 1/Q and 1/t where t is the open-circuit period could be obtained as shown in Figure 24. The extrapolated line to 1/t = 0 intersects close to the charge passed during initial oxidation i.e. the original reactivity can be restored. This observation emphasises the difficulty of attempts to conduct surface analysis studies several hours or days after oxidation using ex-situ equipment. It is therefore not surprising that surface analysis techniques have largely been unsuccessful in identifying the nature of the "passive" surface layer.

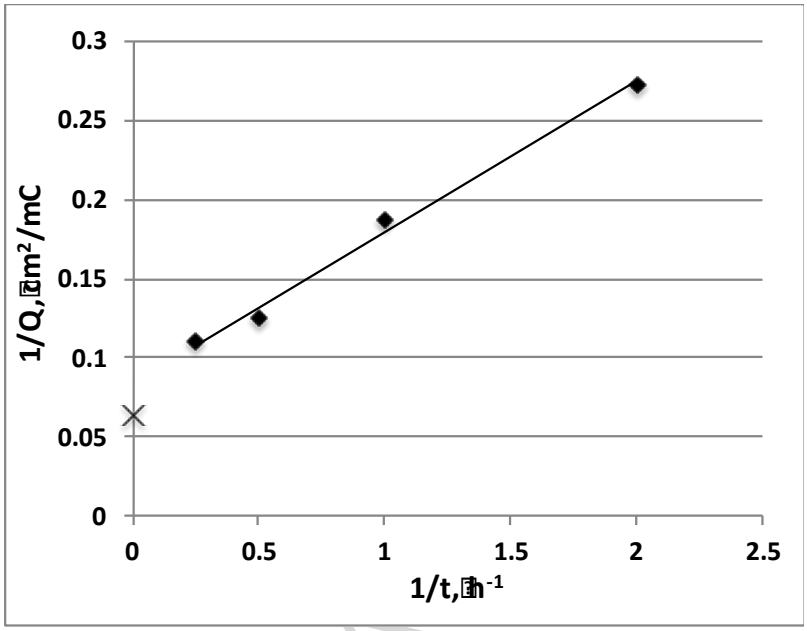

Figure 24. Effect of open-circuit period on charge associated with the transients in Figure 23. The point shown as (X) corresponds to the charge passed in the initial 1h period.

The potentiostatic and coulometric data presented above suggests that oxidative and possibly also non-oxidative dissolution can result in the initial partially selective dissolution of iron resulting in a surface layer which is microscopically very thin and which is enriched in copper. This "passive" so-called polysulfide layer also undergoes anodic dissolution but at a much reduced rate at potentials below the critical potential (approximately 0.9V) and therefore continues to grow in thickness while at the same time, slow solid-state diffusion of iron and copper from the bulk mineral to the surface to restore the original composition limits the current density that can be obtained by oxidation of the mineral at potentials below the critical potential. Oxidation of the passive layer is potential-dependent and this accounts for the effect of potential shown in Figures 13 to 15. The rate increases substantially above the critical potential as will be demonstrated in a subsequent paper. The noticeable effect of pH as shown in Figures 13 to 15 is possibly due to faster oxidation of the copper-rich layer at higher pH values to other sulfur species such as thiosulfate as has previously been suggested (Sand et al, 2001). Thus, writing the polysulfide layer composition as "CuS_2", the following reaction is possible.

$$\text{“}CuS_2\text{”} + 3H_2O = Cu(II) + S_2O_3^{2-} + 6H^+ + 4e \qquad (12)$$

In this regard, it is interesting to note that chalcopyrite does not exhibit such "passivation" behaviour in ammoniacal solutions at high pH values (Moyo et al, 2015) with coulometric measurements indicating formation of thiosulfate as the main product of oxidation of sulfur.

In summary, the results of this study have confirmed that the so-called passivation of the oxidation of chalcopyrite in chloride solutions is, in fact, a slow decrease in anodic reactivity with time that extends beyond 24 hours. The slow growth of a less reactive copper polysulfide layer is suggested as being responsible for this behaviour. It is very likely that this is also true for oxidation in sulfate solutions.

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Highlights

- Mixed potential (E_m) measurements identify the potential region of 0.65 V to 0.8 V important in the leaching process.
- Increase in both E_m with pH increases rate of dissolution.
- Slower rates of dissolution for iron(II) than copper(II) as the oxidant.
- Potentiostatic measurements at various potentials at different pH values have confirmed that chalcopyrite undergoes a slow "passivation" that is not complete even after 24 hours.
- The current densities after prolonged oxidation vary exponentially with potential and increase with increasing pH but are not affected by the concentration of chloride.
- Measurements with chalcopyrite samples from 3 different locations showed only minor variations in anodic reactivity.
- Analysis conducted of both the current-time transients and the re-activation of the mineral surface under zero current conditions after potentiostatic oxidation.
- Results interpreted in terms of a growing copper-rich sulphide layer under anodic polarization.
- Solid-state diffusion through this layer is responsible for the "passivation" process by analogy with the well known similar processes in some binary alloys.